Estimation of the Heat Capacities of Organic Liquids as a Function of Temperature Using Group Additivity: An Amendment

Milan Zábranský and Vlastimil Růžička, Jr.[a)]

Department of Physical Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

An amendment to a second-order group additivity method for the estimation of the heat capacity of pure organic liquids as a function of temperature in the range from the melting temperature to the normal boiling temperature is reported. The temperature dependence of various group contributions and structural corrections is represented by a series of second order polynomial expressions. The group contribution parameters have been developed from an extended database of more than 1800 recommended heat capacity values. The present method should be more versatile and more accurate than the previous one [Růžička and Domalski, J. Phys. Chem. Ref. Data **22**, 597, 619 (1993)] due to the use of a larger database and an improved procedure for parameter calculation. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1797811]

Key words: estimation, group contribution approach, heat capacity of liquids, organic compounds, temperature dependence.

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[a)]Author to whom correspondence should be addressed; electronic mail: vlastimil.ruzicka@vscht.cz

1. Introduction

Heat capacity is a property required for carrying out many chemical engineering calculations, establishing energy balances, or evaluating the effect of temperature on phase and reaction equilibria. As experimental liquid heat capacity data are available for only a fraction of the total number of compounds encountered in industrial processes (02ZAB/RUZ), several estimation methods have been proposed.

In 1993 Růžička and Domalski published two articles (93RUZ/DOM1, 93RUZ/DOM2) describing a method of estimation of the heat capacity of pure organic liquids as a function of temperature. The method was based on the second order additivity scheme proposed by Benson and co-workers for ideal gases (58BEN/BUS, 69BEN/CRU) and for liquid hydrocarbons (77LUR/BEN). The papers (93RUZ/DOM1, 93RUZ/DOM2) were concerned with revision of the existing group contributions and structural corrections developed by Benson and co-workers (69BEN/CRU, 77LUR/BEN) and with the extension of the method to cover a broader range of organic liquids containing elements carbon, hydrogen, oxygen, nitrogen, sulfur, and halogens. Further development of the method was made possible from a large compilation of critically evaluated calorimetrically measured heat capacities (96ZAB/RUZ).

An update of the critically evaluated heat capacity data of organic liquids was published recently (01ZAB/RUZ1). The entire database (96ZAB/RUZ with Erratum 01ZAB/RUZ2 and 01ZAB/RUZ1) of recommended heat capacity data now consists of more than 1800 compounds. With the availability of more data, we have amended the existing group contribution estimation method (93RUZ/DOM1, 93RUZ/DOM2) and developed new parameters covering a larger number of groups and structural units that in some cases are applicable over a broader temperature interval. In addition, a slightly

modified calculational procedure made it possible to estimate parameters describing the temperature dependence of all group contributions and structural units in one step. This should result in a more generally applicable set of group contribution and structural units, and also more accurate estimated heat capacities.

Recently, Chickos *et al.* (93CHI/HES) reported a first order group additivity scheme for estimation of heat capacity values at 298 K. We have compared estimated heat capacities for some selected compounds using this method by Chickos *et al.* with that developed in this work.

2. Development of the Method

2.1. Additivity Scheme

We have used the following expression to estimate the heat capacity of organic liquids:

$$\frac{C}{\mathbf{R}} = \sum_{i=1}^{k} n_i \Delta c_i, \qquad (1)$$

where R is the gas constant ($R = 8.314\,472\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$), (99MOH/TAY), n_i is the number of additivity units of type i, Δc_i is a dimensionless value of the additivity unit of type i, and k is the total number of additivity units in a molecule. The additivity units include groups and structural corrections.

Following the arguments of Růžička and Domalski (93RUZ/DOM1, 93RUZ/DOM2) a simple expression has been chosen for the dependence of Δc_i on temperature

$$\Delta c_i = a_i + b_i \frac{T}{100} + d_i \left(\frac{T}{100}\right)^2, \qquad (2)$$

where T is temperature in K and a_i, b_i, d_i are adjustable parameters. To improve the estimation of heat capacities of 1-alkanols, which exhibit an inflexion point in their dependence of heat capacity with temperature (93ZAB/BUR), a third order polynomial in Eq. (2) was also tested. Even though agreement between experimental and estimated heat capacities for the 1-alkanols improved, the standard residual deviation and the average absolute percent deviation of the overall fit of all data deteriorated. We believe that insufficient accuracy of the heat capacity data and the narrow temperature range of available data for some compounds are the most probable causes preventing the use of a more extensive functional form for the dependence of Δc_i with temperature.

2.2. Temperature Range

The present estimation method is applicable from the melting temperature to the normal boiling temperature, which is the range of the liquid phase most often required in chemical engineering calculations. At present, it is not possible to develop a group contribution method to estimate the heat capacity values of organic liquids over a wider temperature range, as experimental data above the normal boiling temperature are scarce. The present method can be extrapolated to temperatures above the normal boiling point. How-

ever, the predictive accuracy notably deteriorates as the extent of the temperature extrapolation increases. The present method fails near the critical point.

Due to the limited temperature range to which the method is applicable, no distinction is made between the isobaric heat capacity C_p and the saturation heat capacity C_{sat}. At low saturation pressures below 0.1 MPa, C_p and C_{sat} are nearly equal in magnitude. The difference between C_p and C_{sat} at the normal boiling temperature lies typically below 0.5% and the difference becomes significant only at temperatures far above the normal boiling temperature. When the method is applied above the normal boiling temperature the deviations between observed and estimated heat capacities exceed the differences between C_p and C_{sat}.

2.3. Group Notation

We have followed the group notation developed by Benson and co-workers (58BEN/BUS, 69BEN/CRU). The group is defined as a central atom together with its nearest-neighbor atoms and ligands. We have adopted the short form of the notation for multiple bonded atoms (C_d, C_t, C_B, C_{BF}, and C_a) that omits the atom at the other end of the multiple bond. C_d is a double bonded carbon atom attached to a second double bonded carbon atom and to two other monovalent ligands, C_t is a triple bonded carbon atom attached to a second triple bonded carbon atom and to another monovalent ligand, C_B is a carbon atom in a benzene ring attached to two other benzene ring carbon atoms and to another monovalent ligand, C_a is the double bonded carbon atom located in the middle of the allenic group $\rangle C{=}C{=}C\langle$, and C_{BF} is an aromatic ring carbon atom in fused ring aromatic compounds (such as naphthalene or phenanthrene) in the bridge position attached to at least one another C_{BF} atom and from zero to two C_B atoms (for a sample assignment see the paper 93RUZ/DOM1). Table 1 lists 130 groups with computed parameters: 29 contributions for groups containing atoms of carbon and hydrogen; 39 contributions for groups containing atoms of carbon, hydrogen, and oxygen; 20 contributions for groups containing atoms of carbon, hydrogen, and nitrogen; 27 contributions for groups containing atoms of carbon, hydrogen, and halogens; ten contributions for groups containing atoms of carbon, hydrogen, and sulfur, and five contributions for groups containing C and H and mixed halogens or halogens and oxygen.

We have adopted the approach proposed by Benson and co-workers (69BEN/CRU, 76BEN) to estimate the heat capacity of saturated and unsaturated cyclic hydrocarbons (with the exception of aromatic hydrocarbons) and heterocyclic compounds containing oxygen, nitrogen or sulfur. The heat capacity of a cyclic compound is estimated by summing up group contributions developed for acyclic compounds and then adding a structural correction that is specific for the particular cyclic compound. As the corrections reflect the internal ring constraints imposed on a molecule, they are denoted as ring constraints corrections, or rcc. Table 2 lists 24 structural corrections with computed parameters.

Benson *et al.* (69BEN/CRU) and many other authors who have developed a second-order additivity method for the estimation of thermophysical properties arbitrarily assigned values to some groups either when groups exist in conjugate pairs or when data for the calculation of a group are unavailable. We have utilized some of the assignments mainly as it reduced the colinearity of adjustable parameters (94RUZ/DOM). The list of equivalent groups is given in Table 3.

2.4. Next-to-Nearest Neighbor Interactions

The second-order additivity method makes no allowance for next-to-nearest neighbor interactions. Some authors have found that such interactions have considerable influence on molecular properties and therefore included corrections to account for next-to-nearest neighbor interactions. The gauche, *cis*, and *ortho* corrections developed by Benson *et al.* (69BEN/CRU) or the methyl repulsion correction suggested by Domalski and Hearing (88DOM/HEA) are some examples of the approach.

In this work we have developed *cis* and *trans* as well as *ortho* and *meta* corrections as we have used an augmented calculation procedure as compared with the work by Růžička and Domalski (93RUZ/DOM1, 93RUZ/DOM2). Parameter evaluations including the parameters listed above were carried out in a single step. Due to their small magnitude, these corrections were previously neglected (93RUZ/DOM1, 93RUZ/DOM2). The *para* correction has been found to be insignificant. For multisubstituted aromatic hydrocarbons, corrections between all adjacent substituents have been taken into account. Thus, for example, for 1,2,4-trimethylbenzene one *meta* and one *ortho* corrections have been included, for 1,2,3-trichlorobenzene two *ortho* corrections have been included. Values for the corrections are given in Table 2.

3. Determination of Additivity Unit Values

A multiple linear least squares method has been used for the calculation of adjustable parameters in Eq. (2). The minimized objective function has the following form:

$$S = \sum_{j=1}^{m} w_j (C_j^{rec} - C_j^{estd})^2, \qquad (3)$$

where the subscript j denotes jth data point, C_j^{rec} is the recommended liquid heat capacity, and C_j^{estd} is the estimated heat capacity. The weight w_j is equal to the reciprocal of the variance of the jth data point $\sigma^2(C_j)$. It is estimated for each jth value on the basis of the assumed accuracy of the recommended heat capacities. The input information is the percentage error of the recommended data, $\sigma_r C$. Thus, the weight of the jth data point is expressed as

$$w_j = 1 \left/ \left(\frac{C_j \cdot \sigma_r C}{100} \right)^2 \right. . \qquad (4)$$

3.1. Database of Liquid Heat Capacities

The recommended heat capacity values were obtained from an extensive compilation that contains all currently available calorimetrically measured heat capacities of more than 1800 liquid organic compounds (96ZAB/RUZ, 01ZAB/RUZ1). The compilation includes parameters of a smoothing equation obtained from a critical assessment of experimental data. Parameters are accompanied by a rating that represents the expected overall accuracy of the data. The rating was expressed as a percentage error and served as the input information for the calculation of weights in the least squares parameterization [refer to Eq. (4)].

3.2. Parameter Estimation

The adjustable parameters were calculated by simultaneous minimization of the recommended heat capacity values for all selected compounds in one step. Table 4 gives a survey of number of compounds available and those selected, the number of group values evaluated, and the number of ring corrections evaluated. Group values for a total of nine families of compounds were evaluated. Altogether, 555 compounds (hereafter called a ''basic set'' of compounds) have been selected out of 1836 compounds available in the database (96ZAB/RUZ, 01ZAB/RUZ1). The remaining 1281 compounds were rejected for the following reasons: the uncertainty as given in compilations (96ZAB/RUZ, 01ZAB/RUZ1) was above 3%; the recommended values were available only over a limited temperature interval or at a single temperature; and a group or structural contribution would have been calculated from data for only one compound (there were several exceptions to this rule which are given as footnotes under Tables 1 and 2).

In the first step of the calculational procedure all compounds having reliable heat capacity data available over a temperature range of 50 K minimum were selected. Discrete data were generated over a temperature step of 10 K for all selected compounds. The standard deviation (SD) and standard percent deviation (SPD) have been calculated after the minimization procedure:

$$SD = \sqrt{\frac{1}{n_{tot} - n_{par}} \sum_{i=1}^{n_{tot}} (C^{rec} - C^{estd})^2}, \qquad (5)$$

$$SPD = 100 \cdot \sqrt{\frac{1}{n_{tot} - n_{par}} \sum_{i=1}^{n_{tot}} \left(\frac{C^{rec} - C^{estd}}{C^{rec}} \right)^2}, \qquad (6)$$

where n_{tot} is the total number of data points and n_{par} is the number of adjustable parameters in Eq. (2).

All compounds exhibiting large systematic deviations were rejected in the subsequent step of the minimization. Also, for some compounds deviations increased at the beginning or at the end of the temperature interval. This is attributed to the atypical dependency of heat capacity on temperature for some compounds as explained by Zábranský *et al.* (93ZAB/BUR). For such compounds we have either limited the temperature interval of data used in the minimization or

rejected the compound. In the final step, group contribution parameters were calculated using data from the basic set of compounds.

4. Results and Discussion

To evaluate the quality of the group and structural contributions developed, we have used the reliable data from two sources:

(1) data from the database (96ZAB/RUZ, 01ZAB/RUZ1) for those compounds that were not included in the basic set because of a limitation in the temperature range available.

(2) recent data published in the literature following completion of the work by Zábranský *et al.* (01ZAB/RUZ1). Experimental data for a total of 46 compounds coming from the above two sources (hereafter called a "test set" of compounds) were collected and compared to estimated heat capacities using parameters developed in this work. Since selection of compounds in the test set was arbitrary and based mainly on the availability of data, it was impossible to make a relevant statistical evaluation of the results of comparison.

We have also made a comparison with the estimated data by the first order contributions by Chickos *et al.* (93CHI/HES), in this case at 298 K only. Table 5 presents results of the comparison and shows that our percent deviations (PDs) are generally smaller than those of Chickos *et al.* It has been demonstrated that the method by Chickos *et al.*, despite its simplicity of a first order group contribution method, provides reliable estimations.

In previous work (93RUZ/DOM1, 93RUZ/DOM2) the authors have compared the estimated heat capacity values with those calculated by the group contribution method developed by Luria and Benson (77LUR/BEN). Luria and Benson provided contributions only for aliphatic, cyclic, and aromatic hydrocarbons. For these families of hydrocarbons, the SPD [see Eq. (6)] between experimental heat capacities and those estimated by the Luria and Benson method ranged from 1.6% to 3.3%, whereas SPD between experimental heat capacities and those estimated using parameters from Růžička and Domalski (93RUZ/DOM1) ranged from 1.1% to 3.8%. The present method results in SPDs ranging from 0.7% to 1.9% for the same families of compounds. For nine aromatic and cyclic hydrocarbons compounds, there is a lack of group and structural parameters in Luria and Benson; application of the present method has resulted in average deviations ranging from 2.7% to 2.9%.

Some general conclusions have been drawn from the comparison with the test set of compounds. For the majority of compounds the method error lies below 2% at temperatures below the normal boiling temperature and increases with increasing temperature. For alkanols, acids and aldehydes, the error is greater than 3% and rises significantly with increasing temperature. For alkanols the inflexion point in the dependence of heat capacity with temperature rises in the direction of higher temperatures as the number of carbon atoms in the molecule increases. This behavior is difficult to describe using a simple additivity scheme [Eqs. (1) and (2)].

A sharp maximum in the liquid heat capacity curve observed as a function of temperature for some aldehydes cannot be predicted with the present method at all. The estimated heat capacities of some diols are in error by more than 10% (for example 1,6-hexanediol). Moreover, for some diols the estimated heat capacities decrease with increasing temperature or exhibit a maximum in the dependence of heat capacity with temperature, which was not observed experimentally. For these compounds the group contribution method developed in this work should be used for estimating the heat capacity values at and around room temperature only.

Reliable estimations have been obtained for esters with the method error usually below 2%. For halogenated hydrocarbons, the method error was below 1% as shown in Table 5 for a set of 13 compounds. For organic compounds containing sulfur, such as thiols, sulfides, and certain cyclic compounds, the agreement between experimental and estimated heat capacity values is about 1% over a wide temperature range as found for the basic set of compounds (the largest average deviation of 1.8% was obtained for benzenethiol). For amines no recent reliable data were available for comparison. We have therefore used some older data for evaluation where the method error was up to 5%.

It has been found that the accuracy of the present group contribution method deteriorates when applied to multifunctional compounds, i.e. a compound containing functional groups from two or more different families. This is particularly true for multifunctional compounds containing a hydroxyl group (e.g., see N,N′-diethanolamine or 1-chloro-2-propanol in Table 5).

5. Conclusion

Parameters for a group contribution method that permits estimation of heat capacity values of organic liquids have been determined. Summation of group contributions and structural corrections represented by second order polynomials enables the user to obtain an analytical expression for the heat capacity as a function of temperature. The method is applicable for the estimation of heat capacities of liquid organic substances containing atoms of carbon, hydrogen, oxygen, nitrogen, sulfur, and halogens.

The present method cannot be used for the first members of a homologous series; this limitation is typical of a majority of group contributions methods.

It has been demonstrated in previous work (93RUZ/DOM1, 93RUZ/DOM2) that the method can be used to estimate heat capacity values from the melting temperature to the normal boiling temperature; in this range the present group and structural contribution parameters give an overall standard deviation of 6.1 $J \cdot K^{-1} \cdot mol^{-1}$ and overall standard percent deviation of 1.7% (calculated from comparison of recommended and estimated data for the basic set of compounds).

Each group or structural contribution was calculated from the heat capacities for at least two different compounds, with 29 exceptions. Still, there are many group and structural con-

tributions missing as heat capacity data are not available for their evaluation. A short account of the missing heat capacity data for some specific families of compounds is given in Zábranský and Růžička (02ZAB/RUZ).

6. Acknowledgments

7. Appendix. Sample Calculations for the Estimation of the Heat Capacities of Limonene, Ethyl Benzoate, and 1-Chloro-2-Propanol

The structural formula for limonene (1-methyl-4-(1-methylethenyl)cyclohexene) [CAS RN 5989-27-5] is:
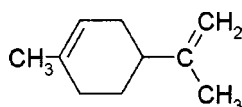
Group additivity representation for limonene: $[2 \times C-(H)_3(C)] + [1 \times C-(H)_2(C)_2] + [1 \times C-(H)(C)_3] + [2 \times C-(H)_2(C)(C_d)] + [1 \times C_d-(H)_2] + [1 \times C_d-(H)(C)] + [2 \times C_d-(C)_2] + [1 \times \text{cyclohexene(rcc)}]$.

Equations (1) and (2) are used to performed the calculation of parameters $a = 18.8512$, $b = 0.757\,816$, $d = 1.041\,75$ valid in the temperature range 171.2–483.1 K. Estimated heat capacity of limonene at 300 K, $C^{\text{estd}}/R = 30.532$ and $C^{\text{estd}} = 253.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Experimental value from (02STE/CHI1) is 250.3 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, PD$= -1.4\%$.

The structural formula for ethyl benzoate [CAS RN 93-89-0] is:
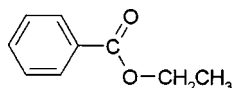
Group additivity representation for ethyl benzoate: $[1 \times C-(H)_3(C)] + [5 \times C_B-(H)(C_B)_2] + [1 \times C_B-(C_B)_2(CO)] + [1 \times C-(H)_2(C)(O)] + [1 \times CO-(C_B)(O)] + [1 \times O-(C)(CO)]$.

Equations (1) and (2) are used to performed the calculation of parameters $a = 22.6571$, $b = 0.715\,298$, and $d = 0.572\,327$ valid in the temperature range 185.0–630.0 K. Estimated heat capacity of ethyl benzoate at 300 K, $C^{\text{estd}}/R = 29.916$ and $C^{\text{estd}} = 248.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Experimental value from (02STE/CHI3) is 244.4 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, PD $= -1.7\%$.

The structural formula for 1-chloro-2-propanol [CAS RN 127-00-4] is:
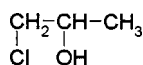
Group additivity representation for 1-chloro-2-propanol: $[1 \times C-(H)_3(C)] + [1 \times C-(H)(C)_2(O)(\text{alcohol})] + [1 \times C-(H)_2(C)(Cl)] + [1 \times O-(H)(C)]$.

Equations (1) and (2) are used to performed the calculation of parameters $a = 24.3205$, $b = -11.1055$, and $d = 3.505\,57$ in the temperature range 188.4–520.0 K. Estimated heat capacity of 1-chloro-2-propanol at 315 K, $C^{\text{estd}}/R = 24.800$ and $C^{\text{estd}} = 200.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Experimental value from (02STE/CHI4) is 206.2 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, PD$= 2.7\%$.

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TABLE 1. Parameters for the dependence of dimensionless group contribution Δc_i on temperature, $\Delta c_i = a_i + b_i(T/100) + d_i(T/100)^2$, T/K

Group	Adjustable parameters			Temperature range
	a_i	b_i/K^{-1}	d_i/K^{-2}	$T_{min}/K - T_{max}/K$
$C-(H)_3(C)$	4.198 45	$-0.312\ 709$	0.178 609	85–705
$C-(H)_2(C)_2$	2.734 5	0.122 732	$-0.123\ 482$	85–700
$C-(H)(C)_3$	$-1.353\ 93$	1.392 18	$-0.101\ 118$	85–483
$C-(C)_4$	$-5.747\ 77$	2.807 27	$-0.314\ 392$	146–423
$C_d-(H)_2$	3.730 72	$-0.213\ 303$	0.143 503	100–580
$C_d-(H)(C)$	4.315 38	$-1.713\ 40$	0.390 372	100–530
$C_d-(C)_2$	0.777 280	$-4.086\ 61 \cdot 10^{-3}$	0.051 210 2	140–580
$C_d-(H)(C_d)$	3.972 88	$-1.709\ 97$	0.473 699	130–553
$C_d-(C)(C_d)$	0.815 385	$-0.445\ 281$	0.222 630	130–580
$C-(H)_2(C)(C_d)$	1.522 45	0.481 876	0.035 342 1	109–530
$C-(H)_2(C_d)_2$	1.895 53	0.296 854	0.092 5396	128–375
$C-(H)(C)_2(C_d)$	$-2.230\ 10$	2.082 99	$-0.240\ 244$	111–460
$C-(C)_3(C_d)^a$	$-5.625\ 56$	2.905 40	$-0.220\ 860$	166–296
$C_t-(H)$	9.667 42	$-4.949\ 89$	1.220 90	150–330
$C_t-(C)$	1.128 84	1.049 79	$-0.178\ 614$	150–284
$C_t-(C_B)$	3.455 50	$-0.528\ 223$	$-0.061\ 362\ 7$	228–330
C_a	3.204 31	$-0.444\ 284$	0.136 136	140–315
$C_B-(H)$	2.216 10	$-0.202\ 639$	0.112 750	170–770
$C_B-(C)$	$-0.168\ 065$	0.644 814	$-0.078\ 899\ 1$	170–700
$C_B-(C_d)$	$-5.217\ 53$	4.873 13	$-0.886\ 240$	228–580
$C_B-(C_B)$	$-5.129\ 97$	4.032 44	$-0.595\ 745$	273–770
$C-(H)_2(C)(C_B)$	2.127 21	0.214 915	0.070 961 5	170–700
$C-(H)_2(C_B)_2$	$-3.825\ 17$	3.966 78	$-0.449\ 402$	268–440
$C-(H)(C)_2(C_B)$	2.415 45	$-1.314\ 92$	0.403 035	180–671
$C-(H)(C_B)_3^a$	$-15.135\ 7$	7.790 76	$-0.855\ 579$	365–596
$C-(C)_3(C_B)$	$-3.493\ 41$	2.005 27	$-0.186\ 897$	170–600
$C_{BF}-(C_{BF})(C_B)_2$	$-4.932\ 52$	3.534 66	$-0.483\ 297$	248–700
$C_{BF}-(C_{BF})_2(C_B)$	$-5.341\ 45$	3.205 83	$-0.375\ 158$	332–510
$C_{BF}-(C_{BF})_3$	23.397 4	$-9.995\ 61$	1.152 91	386–592
$C-(H)_3(O)$	3.703 44	$-1.128\ 84$	0.512 390	130–380
$C-(H)_2(O)_2$	$-0.633\ 479$	0.951 097	$-0.057\ 928\ 4$	171–308
$C-(H)_2(C)(O)$	0.517 007	1.266 31	$-0.093\ 971\ 3$	137–630
$C-(H)_2(C)(CO)$	2.571 78	$-0.054\ 121\ 0$	0.125 804	177–530
$C-(H)_2(CO)_2^a$	$-15.927\ 3$	8.871 01	$-0.755\ 096$	255–360
$C-(H)_2(C_B)(O)$	$-31.731\ 8$	25.099 7	$-4.325\ 61$	260–462
$C-(H)(C)_2(O)$ (ether)	$-2.325\ 91$	1.949 30	$-0.183\ 551$	130–520
$C-(H)(C)_2(O)$ (alcohol)	$-4.644\ 39$	2.389 89	0.172 814	188–630
$C-(H)(C)_2(CO)$	1.348 04	$-1.104\ 64$	0.388 707	184–510
$C-(C)_2(O)_2^a$	$-9.669\ 43$	8.452 10	$-1.344\ 17$	273–334
$C-(C)_3(O)$ (ether)^a	$-5.558\ 59$	2.736 81	$-0.295\ 802$	168–308
$C-(C)_3(O)$ (alcohol)	$-62.739\ 9$	42.483 7	$-6.519\ 40$	220–453
$C-(C)_3(CO)$	$-5.771\ 66$	2.892 98	$-0.347\ 793$	226–370
$C_d-(H)(CO)$	15.001 6	$-2.386\ 63$	$-0.502\ 618$	205–580
$C_d-(C)(CO)$	33.196 5	$-15.545\ 1$	1.768 77	199–428
$C_B-(C_B)_2(O)$	11.708 9	$-4.327\ 18$	0.534 999	277–600
$C_B-(C_B)_2(CO)$	$-12.835\ 5$	8.669 59	$-1.283\ 13$	185–705
$CO-(H)(C)$	13.365 6	$-5.293\ 94$	1.096 33	177–428
$CO-(H)(C_d)$	17.137 8	$-6.898\ 75$	1.061 18	218–428
$CO-(C)_2$	6.315 05	0.347 175	$-0.179\ 791$	184–383
$CO-(C)(C_d)$	$-3.476\ 65$	0.307 623	0.816 128	273–580
$CO-(C)(C_B)^a$	17.868 8	$-7.096\ 95$	0.981 906	298–680
$CO-(H)(O)$	13.319 3	$-0.803\ 329$	1.701 59	275–342
$CO-(C)(O)$	8.081 78	$-0.089\ 984\ 5$	1.824 52	189–510
$CO-(C_d)(O)$	$-13.702\ 0$	6.873 82	1.766 44	199–415
$CO-(C_B)(O)$	17.748 1	$-7.855\ 02$	3.214 63	185–705
$CO-(O)(CO)$	2.059 55	1.839 94	1.794 33	318–347
$CO-(O)_2$	14.452 8	$-4.954\ 51$	4.792 74	270–510
$O-(H)(C)$	16.155 5	$-11.938\ 0$	2.851 17	153–590
$O-(H)(C)$ (diol)	$-3.914\ 14$	5.372 48	$-0.725\ 920$	240–630
$O-(H)(C_B)$	$-6.132\ 29$	7.340 47	$-0.950\ 215$	285–490
$O-(H)(CO)$	$-2.037\ 28$	0.661 816	$-1.582\ 48$	241–510
$O-(C)_2$	6.353 42	$-0.969\ 836$	$-0.037\ 828\ 5$	130–520
$O-(C)_2$ (alcohol)	0.328 815	5.509 07	$-1.456\ 65$	273–460
$O-(C)(C_d)^a$	6.724 03	$-1.808\ 59$	0.275 264	320–500
$O-(C)(C_B)$	$-12.521\ 7$	11.579 5	$-2.072\ 31$	277–520
$O-(C_B)_2$	$-29.686\ 4$	16.166 3	$-2.206\ 94$	191–570

TABLE 1. —Continued

Group	Adjustable parameters			Temperature range
	a_i	b_i/K^{-1}	d_i/K^{-2}	$T_{\min}/\text{K} - T_{\max}/\text{K}$
O–(C)(CO)	1.948 51	−0.039 677 5	−2.007 56	185–705
O–(C$_d$)(CO)[a]	−2.374 55	1.285 61	−1.952 13	189–330
C–(H)$_3$(N)	6.666 28	−3.047 69	0.803 453	161–388
C–(H)$_2$(C)(N)	5.657 28	−1.814 84	0.312 815	190–590
C–(H)(C)$_2$(N)	−3.276 77	3.322 81	−0.505 009	181–398
C–(C)$_3$(N)	−0.104 392	0.334 373	−0.031 8456	210–398
C$_B$–(C$_B$)$_2$(N)	5.723 48	−2.183 15	0.317 372	235–770
N–(H)$_2$(C)	9.769 72	−0.787 001	0.029 084 4	181–770
N–(H)$_2$(N)	6.691 10	−0.535 766	0.116 779	216–464
N–(H)(C)$_2$	−8.479 43	13.729 3	−2.839 67	185–590
N–(H)(C)(C$_B$)[a]	−8.672 23	9.648 76	−1.684 57	240–379
N–(H)(C)(N)	2.911 50	2.655 01	−0.604 121	205–298
N–(H)(C$_B$)(N)[a]	−5.304 32	6.363 28	−0.997 913	293–358
N–(H)(C$_B$)$_2$ (pyrrole)	−22.444 0	15.416 5	−1.984 31	256–441
N–(C)$_3$	−5.184 09	7.145 55	−1.555 46	161–590
N–(C)$_2$(C$_B$)[a]	−15.723 4	13.261 7	−2.488 03	283–388
N–(C)$_2$(N)	−2.832 75	6.326 87	−1.338 94	205–298
N$_B$–(C$_B$)$_2$	0.664 604	1.293 87	−0.194 972	207–610
C–(H)$_2$(C)(CN)	10.219 5	−1.195 19	0.303 634	185–370
C–(C)$_3$(CN)[a]	1.517 27	3.439 98	−0.535 832	296–346
C$_d$–(H)(CN)[a]	9.516 81	−1.130 73	0.287 598	197–347
C$_B$–(C$_B$)$_2$(CN)	−1.004 35	4.620 53	−0.659 838	265–480
C$_B$–(NCO) (isocyanate)	5.350 72	2.012 31	−0.246 140	242–480
C$_B$–(C$_B$)$_2$(NO$_2$)	35.655 1	−14.442 6	1.957 94	250–415
C–(H)$_2$(C)(NO$_2$)[a]	17.940 8	−5.313 96	1.035 48	189–300
O–(C)(NO$_2$)	15.999 8	−4.748 18	1.077 20	191–300
C–(H)$_2$(C)(Br)	10.339 4	−1.288 15	0.189 034	222–360
C–(H)$_2$(C)(Cl)	8.610 93	−1.244 70	0.302 973	140–520
C–(H)$_2$(C$_B$)(Cl)[a]	18.649 9	−7.808 96	1.408 52	246–347
C–(H)$_2$(C)(F)	5.649 21	−0.221 284	0.284 400	173–308
C–(H)$_2$(C)(I)	−0.758 309	5.813 19	−0.933 958	243–345
C–(H)(C)$_2$(Br)	7.037 71	−0.513 121	0.114 302	190–475
C–(H)(C)$_2$(Cl)	5.146 01	0.208 322	0.053 585 2	182–520
C–(H)(C)(Cl)$_2$	6.998 87	2.512 47	−0.498 986	123–330
C–(H)(C)(Cl)(F)[a]	6.232 24	0.236 507	0.286 196	105–328
C–(H)(C)(Cl)(O)[a]	−5.976 73	5.529 10	−0.380 660	300–335
C–(H)(C)(F)$_2$	13.180 3	−5.548 67	1.341 16	163–360
C–(C)(Br)(F)$_2$	9.140 28	−0.464 167	0.297 157	166–413
C–(C)$_3$(Cl)	5.327 42	−0.615 941	0.096 141 2	189–306
C–(C)$_2$(Cl)$_2$[a]	7.007 61	1.656 18	−0.357 188	240–267
C–(C)(Cl)$_3$	10.260 4	1.176 06	−0.141 100	240–310
C–(C)(Cl)(F)$_2$	9.509 84	−1.506 26	0.535 196	123–420
C–(C)(Cl)$_2$(F)	13.889 1	−2.691 96	0.554 294	105–420
C–(C)$_2$(F)$_2$	−1.114 36	5.200 58	−0.911 666	126–380
C–(C)(F)$_3$	5.155 30	0.810 691	0.352 253	126–380
C–(C$_B$)(F)$_3$	16.263 5	−6.372 27	1.259 70	211–365
C$_d$–(H)(Cl)[a]	7.453 74	−0.909 389	0.169 918	119–300
C$_d$–(Cl)(F)[a]	7.996 76	−0.931 574	0.272 285	120–240
C$_d$–(Cl)$_2$	10.415 8	−2.215 28	0.589 100	157–291
C$_d$–(F)$_2$	7.461 38	−1.818 50	0.739 347	120–240
C$_B$–(C$_B$)$_2$(Br)	1.936 83	1.961 56	−0.261 815	243–369
C$_B$–(C$_B$)$_2$(Cl)	7.395 60	−1.951 70	0.368 160	230–437
C$_B$–(C$_B$)$_2$(F)	1.724 66	1.339 75	−0.149 748	211–490
C$_B$–(C$_B$)$_2$(I)[a]	2.769 62	2.816 71	−0.563 751	250–320
C–(H)$_3$(S)	12.508 3	−4.370 48	−1.117 39	167–369
C–(H)$_2$(C)(S)	9.826 04	−3.380 11	−1.321 66	130–440
C–(H)(C)$_2$(S)	6.938 21	−2.427 95	−1.465 61	135–490
C–(C)$_3$(S)	4.527 61	−1.852 76	−1.568 62	172–364
C$_B$–(C$_B$)$_2$(S)	2.228 65	0.466 465	−1.966 73	239–700
S–(H)(C)	2.054 73	1.182 07	1.739 90	130–375
S–(C)$_2$	−8.988 55	6.242 28	2.831 03	166–700
S–(C$_B$)(C)[a]	−3.041 52	3.496 85	3.221 18	261–321
S–(C$_B$)$_2$ (thiophene)	5.778 42	−1.044 58	0.184 344	207–344
S–(C)(S)	−1.516 60	2.448 92	1.519 85	168–352

[a]Adjustable parameters were calculated from heat capacity data on a single compound only.

TABLE 2. Parameters for the dependence of dimensionless structural correction Δc_i on temperature, $\Delta c_i = a_i + b_i(T/100) + d_i(T/100)^2$, T/K

	Adjustable parameters			Temperature range
Structural correction	a_i	b_i/K^{-1}	d_i/K^{-2}	$T_{min}/K - T_{max}/K$
Cyclopropane[a]	4.266 04	−3.843 65	0.918 892	154−315
Cyclobutane	3.603 13	−3.925 27	0.896 841	140−301
Cyclopentane	0.256 206	−1.255 79	0.213 503	140−460
Cyclohexane	−1.423 09	−0.688 726	0.164 691	144−490
Cycloheptane[a]	−11.018 2	5.423 84	−0.864 357	269−300
Cyclooctane[a]	−11.581 4	6.220 87	−0.987 897	295−322
Cyclopentene	0.137 841	−1.099 12	0.279 412	141−460
Cyclohexene	−3.571 80	1.084 91	−0.044 809 0	171−700
Cyclohexadiene	−8.828 41	7.250 33	−1.533 56	170−300
Indan	0.481 775	−0.555 782	0.112 688	170−394
1H-indene[a]	−3.287 73	2.482 45	−0.442 470	280−375
Hexahydroindan	−0.366 075	−1.900 51	0.374 255	212−483
Tetrahydronaphthalene[a]	−8.874 95	5.046 17	−0.707 983	248−660
Decahydronaphthalene	−5.976 05	1.261 83	−0.175 636	234−483
Ethylene oxide	10.327 6	−8.257 74	1.719 76	150−520
1,3-Dioxolane	−3.189 59	0.855 281	−0.016 283 9	176−350
Furan	33.969 2	−17.457 1	2.537 50	191−307
Tetrahydrofuran	−0.975 198	−2.139 99	0.633 211	190−410
Tetrahydropyran	−34.549 2	22.483 3	−3.810 53	265−327
Pyrrolidine	12.637 6	−11.787 8	2.411 12	190−400
Piperidine	25.660 7	−20.598 0	3.794 22	267−370
Thiacyclobutane[a]	0.952 952	−1.984 37	0.485 018	202−321
Thiacyclopentane	−3.067 25	0.779 155	0.010 520 9	180−389
Thiacyclohexane[a]	−1.094 44	1.385 72	−1.865 79	296−342
Cis-	0.368 104	−0.427 315	0.119 276	129−423
Trans-	−2.082 09	1.873 29	−0.378 337	170−553
Ortho-	−0.553 312	0.419 661	−0.069 9794	185−600
Meta-	−2.421 14	1.460 18	−0.225 513	214−705

[a]Adjustable parameters were calculated from heat capacity data on a single compound only.

TABLE 3. List of equivalent groups

$C-(H)_3(C) \equiv C-(H)_3(C_d) \equiv C-(H)_3(C_t) \equiv C-(H)_3(C_B) \equiv C-(H)_3(CO) \equiv C-(H)_3(S)$
$C-(H)_2(C)(C_t) \equiv C-(H)_2(C)(C_d)$
$C_B-(C_t) \equiv C_B-(C_d)$
$C_d-(H)(C_B) \equiv C_d-(H)(C_d)$
$C_d-(C)(C_B) \equiv C_d-(C)(C_d)$
$C_B-(C)(C_B)(C_{BF}) \equiv C_B-(C)$
$C_B-(C_t)(C_B)_2 \equiv C_B-(C_d)(C_B)_2$
$N-(H)_2(C_B) \equiv N-(H)_2(C)$
$S-(H)(C_B) \equiv S-(H)(C)$
$O-(H)(C_B)$ (diol) $\equiv O-(H)(C)$ (diol)
$CO-(H)(C_B) \equiv CO-(H)(C_d)$
$C-(H)_2(C_d)(Cl) \equiv C-(H)_2(C)(Cl)$
$C-(H)_2(C_B)(N) \equiv C-(H)_2(C)(N)$
$N-(C)(C_B)_2 \equiv N-(C)_3$
$C-(H)_2(C_d)(O) \equiv C-(H)_2(C_B)(O)$
$S-(C_B)(S) \equiv S-(C)_2$
$S-(C_B)_2 \equiv S-(C)_2$

TABLE 4. Survey of available and selected compounds

Family of compounds	Number of compounds in the database	Number of selected compounds used in the parameter calculation	Number of developed group contributions	Number of developed structural rcc corrections
Hydrocarbons	377	163	29	14
Compounds of C, H, and O	552	183	39	5
Compounds of C, H, and N	165	57	20	2
Compounds of C, H, and S	63	45	10	3
Compounds of C, H, and halogens	229	78	27	0
Compounds of C, H, O, and halogens	55	5	1	0
Compounds of C, H, O, N and F	215	24	4	0
Compounds of C, H, O and S	8	0	0	0
Other compounds	172	0	0	0
Total	1836	555	130	24[a]

[a]Four more structural corrections (*cis, trans, ortho, meta*) have been developed.

TABLE 5. Comparison of experimental and estimated heat capacities for the test set of compounds

Compound	Reference to experimental data	Temperature range for comparison/K	PD[a]/%	PD[a] at 298 K (%) This work	PD[a] at 298 K (%) Method 93CHI/HES
3,3-Dimethylhexane	47OSB/GIN	290–305	−1.9 to +1.6	+0.1	−1.1
Tridecane	54FIN/GRO	270–310	+4.3 to +1.8	+2.2	−3.4
1-Nonene	90MES/TOD	200–380	+2.9 to −3.7	+0.2	−3.5
4-Methyl-1-pentene	94LEB/SMI			−0.5	+2.5
Ethylidenecyclohexane	79FUC/PEA			+1.7	−4.7
(1,1-Dimethylethyl)benzene	02STE/CHI4	298–380	−1.8 to −3.0	−1.8	−0.8
(1-Methylpropyl)benzene	02STE/CHI4	298–400	−0.3 to −5.6	−0.3	−2.0
Limonene[b]	02STE/CHI1	298–360	−1.3 to −1.7	−1.3	−3.8
2-Methyl-2-(1-methyloxy)propane	01VAR/DRU	190–320	−1.6 to +1.5	+1.3	+2.2
2-Methyl-2-propoxypropane	01VAR/DRU	190–320	−3.6 to +0.4	−0.4	−1.4
2-Methoxy-2-methylbutane	02STE/CHI1	300–500	−0.8 to −3.7	−0.8[c]	−0.3
Dibutoxymethane	00PAL/SZA	298–310	+1.0 to +5.5	+1.0	−9.3
1,2-Dimethoxybenzene	01BEC/GME	310–360	−3.4 to +2.4		
Triglyme[d]	01BEC/GME	310–410	+1.2 to +3.5		
1-Hexanol	03VAN/GAB	240–380	+1.9 to +0.4	+3.1	−2.8
1-Octanol	03VAN/GAB	260–380	+4.7 to +3.8	+5.5	−1.0
1-Dodecanol	03VAN/VAN	298–380	+8.0 to +4.6	+8.0	+0.7
1-Heptadecanol	03VAN/VAN	330–370	+9.4 to +7.1		
1-Eicosanol	01VAN/OON2	340–360	+9.6 to +8.1		
1,2-Propanediol	02STE/CHI5	300–540	−2.9 to −4.7	−2.9[c]	−2.3
1,3-Propanediol	02TSV/KUL	250–298	−2.4 to −2.0	−2.0	−14.3
1,6-Hexanediol	91STE/CHI	313–413	+3.8 to +15.6		
trans-2-Butenal[e]	02STE/CHI1			+0.1	−1.5
5-Hexen-2-one	02STE/CHI6	300–380	−0.1 to −0.3	−0.1[c]	+0.1
2-Ethylhexanal	01BEC/GME	310–380	−1.2 to −8.3		
1,5-Pentanedioic acid	02STE/CHI3	370–480	+2.9 to −9.6		
Cyclohexyl formate	01KOZ/BLO	270–310	−6.4 to −2.1	−3.0	[f]

TABLE 5. —Continued

Compound	Reference to experimental data	Temperature range for comparison/K	PD[a]/%	PD[a] at 298 K (%) This work	PD[a] at 298 K (%) Method 93CHI/HES
Cyclohexyl acetate	01KOZ/BLO	240–298	−3.7 to −1.7	−1.7	−1.1
Cyclohexyl pentanoate	01KOZ/BLO	230–310	−4.1 to −4.2	−4.4	−6.3
Methyl benzoate	02BLO/PAU	270–298	−0.1 to −1.5	−1.5	−2.8
Methyl 2-methylbenzoate	02BLO/PAU	230–298	+2.2 to −2.5	−2.5	−6.1
Methyl 3-methylbenzoate	02BLO/PAU	280–298	+0.9 to +0.8	+0.8	−3.5
Ethyl trimethylacetate	02STE/CHI2	300–360	−2.4 to +1.4	−2.4[c]	+0.1
Ethyl benzoate	02STE/CHI3	300–500	−1.8 to −2.6	−1.8[c]	−4.4
Diethyl carbonate	01BEC/GME	310–410	−2.2 to +0.4		
Octyl acetate	01BEC/GME	310–420	−1.8 to +1.4	−1.7[c]	−3.9
Triethylene glycol[e,g]	02STE/CHI5	300–320	+1.4 to +4.5	+1.4[c]	−6.9
N-(Methylethyl)-2-propanamine	99ZIJ/WIT	278	+4.7		
N-Propyl-1-propanamine	91PES/NIK			+1.6	+1.7
1-Decanamine	77BEL/BUB			+5.8	+0.2
N,N-Dimethylbenzenamine	96ZAB/RUZ			−0.1	−2.1
4′-Propylbiphenyl-4-carbonitrile	91ASH/SOR	340–380	+3.6 to +3.8		
Pyrazine	03CHI/KNI	330–540	−2.3 to +3.2		
4-Bromotoluene	96VAN/ALV	300–320	−0.9 to −1.0	−0.9[c]	−7.4
1,2-Dichloroethane	03GOR/TKA	284–328	+2.3 to +2.1	+2.1	+2.8
1,3-Dichloropropane	03GOR/TKA	284–328	+1.1 to +3.0	+1.2	−0.2
1,4-Dichloropropane	03GOR/TKA	284–328	−0.0 to −0.3	+0.1	−3.0
1,5-Dichloropentane	03GOR/TKA	284–328	+0.1 to −0.2	+0.0	−4.0
1,6-Dichlorohexane	03GOR/TKA	284–328	−0.4 to −0.7	−0.4	−5.2
2-Chlorobutane	93SHE			−0.2	+3.7
4-Chlorotoluene	96VAN/ALV			+0.2[c]	−3.9
1,4-Difluorobenzene	91LIC			−0.5	+5.5
Decafluorobiphenyl	71PAU/RAC	349	−0.1		
4-Iodotoluene	96VAN/ALV	310–330	−1.1 to −0.3		
1,4-Bromoiodobenzene	01VAN/OON1	365[h]	+2.0		
1-Chloro-2-propanol	02STE/CHI4	315–355	−2.7 to −11.4		
Dicamba[i]	01DI/LI	392–402	−2.2 to −0.8		
N,N′-Diethylethanolamine	02STE/CHI6	298–450	+12.3 to 3.8	+12.3	+5.7
1-Nitropropane	96TAN/TOY			−1.7	+1.9
2-(2-Aminoethoxy)ethanol	99CHI/LIU	303–353	+3.1 to +0.9	+3.2[c]	+4.4
Pentafluoroaniline	69PAU/LAV	318	−3.4		
2-Bromothiophene	93FUJ/OGU1	240–298	−0.1 to −1.9	−1.9	−5.4
2-Chlorothiophene	93FUJ/OGU2	230–298	−2.5 to −1.44	−1.4	−6.2
Thiazole[j]	68GOU/WES	240–340	−3.7 to +2.9	−2.7	−4.4

[a]Percent deviation PD$=100[(C^{exp}-C^{estd})/C^{exp}]$, where C^{exp} is the experimental liquid heat capacity, C^{estd} is the estimated heat capacity.

[b]1-Methyl-4-(1-methylethenyl)cyclohexene.

[c]Experimental data extrapolated to 298 K.

[d]1,2-Bis[2′-methoxyethoxy]ethane.

[e]The estimation method may be used around 300 K only. The estimated heat capacities decrease with increasing temperature contrary to experimental data which monotonically increase.

[f]The method by 93CHI/HES does not include a group value required for the estimation.

[g]2,2′-(Ethylenedioxy)diethanol.

[h]Upper limit of the estimated value valid to 320 K only; extrapolated to 365 K.

[i]3,6-Dichloro-2-methoxybenzoic acid.

[j]The estimated heat capacity was obtained by summing up three $C_B-(H)$ and one $N_B-(C_B)_2$ and one $S-(C_B)_2$ thiophene contributions.